USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 380
PURGEABLE HYDROCARBONS BY GC FID

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1 SCOPE AND APPLICABILITY

This method describes the procedures used to determine total petroleum hydrocarbons as gasoline (TPH-g) in water and solid matrices.

This SOP is based on procedures from EPA SW 846: Method 5030C Revision 3, May 2003; Method 5035A Draft Revision 1, July 2002; and Method 8015C Revision 3, February 2007. Deviations from reference methods are described in Appendix A.

Analytes and quantitation limits are provided by matrix in Appendix B.

2 METHOD SUMMARY

An inert gas is bubbled through a portion of an aqueous sample (or methanol extract from solid samples). Volatile organic compounds are vaporized and swept through a sorbent column where they are adsorbed. The sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column. A temperature program is used in the gas chromatograph to separate the organic compounds followed by detection using a flame ionization detector (FID).

TPH as gasoline is quantitated by determining the retention times of 2-methylpentane and 1,2,4-trimethylbenzene and using these markers to establish the retention time range of the gasoline. The area sum response of the sample over this retention time range is compared to the area sum response of gasoline standards analyzed under the same conditions as the sample. If required, probable identification of gasoline in samples is done by comparing the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of gasoline analyzed under the same conditions as the standard. The identification of TPH as gasoline may be complicated by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type.

3 DEFINITIONS

Analytical Sample - Any sample in which analytes are being determined, excluding standards, blanks, or QC reference samples.

Continuing Instrument Calibration Verification (CCV) – A standard containing the analytes of interest, which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence.

FID - Flame Ionization Detector.

Initial Calibration Standards (ICAL) – Standards used to calibrate the instrument response

with respect to analyte concentration.

Instrument Blank (IB) - A blank that is the same matrix as the calibration standards, but without the analytes.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS - Laboratory Information Management System. The Element database.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as laboratory fortified matrix (LFM).

Matrix Spike Duplicate (MSD) – A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added. The MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The MSD is also known as laboratory fortified matrix duplicate (LFMD).

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

PID – Photo Ionization Detector.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks.

Quantitation Limit Standard (QLS or LCV) - A standard used to check the accuracy of the analysis at the quantitation limit. Equivalent to the lowest level calibration standard.

RT – retention time.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration. The SCV is also known as quality control sample (QCS).

Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, solid, sludge, or sediment.

Stock Standard Solution (SSS) - A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Storage Blank (SB) – An aliquot of reagent water stored with samples in the sample storage refrigerator. The storage blank indicates whether contamination may have occurred during sample storage.

Surrogate Analyte (SA or SURR) - An analyte which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

TPH - Total Petroleum Hydrocarbon.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, groundwater, storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and

exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including laboratory coats, safety glasses, and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required. Refer to the Material Safety Data Sheets located in the library and the LAN for additional information.

4.1.1 Methanol

Methanol is the primary solvent used for the preparation of standards and for soil sample extraction in these procedures. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing, and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in a laboratory fume hood with appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammable storage cabinet away from oxidizers and sources of ignition.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC and autosampler operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample extracts, methanol portion	Hazardous Waste	Flammable
Regulated solid sample waste (spent samples, glass vials, etc.)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Aqueous samples should be collected in 40-mL VOA vials and preserved with HCl to pH <2.

Soil samples should be collected using one of the following methods:

1. Collect sample in 5g EnCore™ samplers and cool to 4 ± 2 °C (or freeze to < -7°C and ≥ -20°C) for no more than 48 hours, then preserve upon laboratory receipt.
2. Extrude the sample into a tared 40 mL VOA vial, cap immediately and cool to 4 ± 2 °C (or freeze to < -7 °C and ≥ -20 °C) for no more than 48 hours then preserve upon laboratory receipt.
3. Extrude the sample into a tared 40 mL VOA vial containing methanol for medium level analysis and cool to 4 ± 2 °C.

Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. Three VOA vials of water or three 5 g aliquots of solid sample should be sufficient to meet these objectives. Note that a separate 10 g aliquot of solid material should be provided for moisture determination.

5.2 Internal Chain-of-Custody

The sample custodian delivers water samples to a sample refrigerator in Room 201 or other area where the samples will be analyzed. The sample custodian delivers solid samples to a sample freezer in Room 201 or other area where the samples will be analyzed.

Verify sample IDs and dates of collection against the chain-of-custody form.

5.3 Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location the appropriate room number. When finished with the samples, return sample containers and excess aliquots to the designated sample locations. Update the LIMS database to change the container disposition to "available in" and use the "return to home location" designation to update sample location.

5.4 Preservation Verification

Water samples must be analyzed within 7 days of sampling; preserved water samples must be analyzed within 14 days of sampling.

Solid samples must be extracted within 48 hours of sampling following Section 8.3.2. Sample extracts must be analyzed within 14 days.

5.5 Sample Storage

Store water samples in a refrigerator maintained at > 0 °C to 6 °C.

Store solid samples and sample extracts as outlined in section 5.1.

6 INTERFERENCES

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms, or by carryover when low concentration extracts are analyzed after high concentration extracts.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

6.1 Carryover

Contamination by carryover can occur whenever high level and low level samples are analyzed in sequence. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses.

For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging vessel with a detergent solution between analyses, rinse it with distilled water, then methanol. Dry in an oven at 105 °C. In addition, purge an aliquot of methanol through the affected port. Analyze reagent water blank to show that the port is not contaminated before analyzing further samples. The trap and other parts of the system

are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Analytical balance - capable of measuring differences of 0.01 g.
- Gas chromatograph equipped with a FID detector (or PID/FID in series) and a splitless injection port (Hewlett Packard 5890 Series II gas chromatograph, Agilent AG6890 gas chromatograph, or equivalent).
- Data Acquisition and Processing System - able to control the GC and to acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).
- Fused Silica Capillary Gas Chromatography Column - 75m x 0.53mm x 3µm RTX-624 wide bore capillary column (Restek part # 10974 or equivalent). Any capillary column that provides adequate resolution, capacity, accuracy, and precision, may be used. The column is interfaced to the purge and trap device (OI Analytical, Tekmar 3100, or equivalent).
- Purge and trap concentrator. (OI 4560, Tekmar 3000 purge and trap concentrator, or equivalent.)
- Autosampler: OI DPM-16, Varian Archon, or equivalent.
- Tenax trap (OI #7) or VOCARB 3000 type K, – alternate traps may be used provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision.

7.2 Reagents

Record purchased reagents, such as methanol, in the Region 9 laboratory information management system (LIMS).

- Methanol, Burdick and Jackson purge and trap grade (232-1) or equivalent.

- Reagent Water: All references to water in this method refer to water in which method analytes or other interferences are at less than one-half the QL of the analytes of interest. The Region 9 Laboratory organic-free deionized water is further cleaned by bubbling contaminant-free inert gas through the water.

- Reagent Sand - Sand, sea washed (VWR Cat. #VW3358-3 or equivalent). Bake at 400°C for at least 1 hour before use. Store in a closed container.

7.3 Standards

All standards must be entered into the Region 9 LIMS.

Store unopened ampulated stock standard solutions, and all working standard solutions in glass bottles or vials with Teflon lined screw caps, at ≤-10 °C. Protect all standards from light. Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months or sooner if QC results indicate a problem.

Opened ampules of standards must be discarded six months after opening or earlier if evidence of degradation is observed. LIMS expiration dates must be revised when ampules are opened if the remaining time on the vendor expiration date exceeds six months. The vendor expiration date should be recorded in the comment portion of the standard record.

The following solution concentrations are recommended only; other concentrations can be used.

CAUTION: Allow all standard solutions to equilibrate to room temperature before use.

- Gasoline Stock Standard: Restek #30205 (XHc Unleaded Gasoline Composite Standard at 50,000 µg/mL) or equivalent.

- Gasoline Primary Dilution Standards (PDS): Prepare a solution by diluting the Gasoline Stock Standard to concentration of 100 µg/mL in P&T methanol (20 uL to 10 mL) when using the OI autosampler, and 1,000 µg/mL in P&T methanol (200 uL to 10 mL) when using the Archon autosampler, or equivalent.

- SCV Stock Standard: Supelco # 47519-U (Gasoline at 20,000 µg/mL) or equivalent.

- SCV Primary Dilution Standards (SCVPDS): Prepare a solution by diluting the SCV Stock Standard to concentration 100 µg/mL in P&T methanol (50 uL to 10 mL)), or equivalent, when using the OI autosampler.

- Window Defining Standard (WDS): AccuStandard Custom Mix S-10760-2.5X or equivalent. This solution contains 2-methylpentane and 1,2,4-trimethylbenzene at 5,000 µg/mL in methanol.

- WDS Primary Dilution Standards (WDSPDS): Prepare by diluting the WDS standard to 100 µg/mL in P&T methanol (200 uL to 10 mL), or equivalent.

- Surrogate Spike: Restek #30068, solution of α,α,α-trifluorotoluene in methanol at 2,500 µg/mL, or equivalent.

- Water Surrogate Spike: Prepare a solution by diluting the Surrogate Spike Solution Stock Standard to concentration of 125 µg/mL in P&T methanol (500 uL to 10 mL), or equivalent, when using the OI autosampler, and 625 µg/mL in P&T methanol (500 uL to 2 mL), or equivalent, when using the Archon autosampler.

- Soil Matrix Spike/LCS Solution: the soil matrix spike/LCS solution is Gasoline Stock Standard at 50,000 µg/mL.

- Water Matrix Spike/LCS Solution: the water matrix spike/LCS solution is Gasoline PDS Standard at 100µg/mL.

- Calibration Verification (CCV) - Equivalent to the mid-point initial calibration solution: 500 µg/L.

- Quantitation Limit Standard (QLS) - Equivalent to the lowest level calibration standard: 50 µg/L.

- Second Source Verification (SCV) - Equivalent to the mid-point initial calibration solution, 500 µg/L but prepared from a source different from the source of calibration standards (use SCV Primary Dilution Standards (SCVPDS) to make this standard).

- Site specific hydrocarbon standards may also be supplied by the project manger for use in the laboratory.

7.3.1 Calibration Solutions

The following calibration solution concentrations are typical concentrations only; other concentrations may be used. Use of gastight syringes is required for sample and standard preparation.

When using the OI autosampler:

- Prepare the calibration standards by adding the following solutions to 5 mL of water in a gastight syringe prior to injecting the resulting solution into the OI sparge tube.

QC Type	Solution	Conc. µg/mL	Volume Used, µL	Final Volume, mL	Final Conc., µg/L
WDS	WDSPDS	100	25	5	500
	Surrogate Spike	125	5	5	125
ICAL 1	PDS Solution	100	2.5	5	50
QLS	Surrogate Spike	125	5	5	125
ICAL 2	PDS Solution	100	5	5	100
	Surrogate Spike	125	5	5	125
ICAL	PDS Solution	100	25	5	500
3/CCV/LCS	Surrogate Spike	125	5	5	125
ICAL 4	PDS Solution	100	50	5	1,000
	Surrogate Spike	125	5	5	125
ICAL 5	PDS Solution	100	100	5	2,000
	Surrogate Spike	125	5	5	125
SCV	SCV PDS	100	25	5	500
	Surrogate Spike	125	5	5	125

When using the Archon autosampler:

- Prepare the calibration standards by adding the following solutions to 50 mL of water in a syringe to make standards at recommended concentrations prior to mixing and transferring the resulting solution to a 40 ml VOA vial and loading the vial onto the Archon autosampler.

QC Type	Solution	Conc. µg/mL	Volume Used, µL	Final Volume, mL	Final Conc., µg/L
WDS	WDSPDS	100	25	5	500
ICAL 1 QLS	PDS Solution	100	2.5	5	50
ICAL 2	PDS Solution	100	5	5	100
ICAL 3/CCV/LCS	PDS Solution	100	25	5	
ICAL 4	PDS Solution	100	50	5	1,000
ICAL 5	PDS Solution	100	100	5	2,000
SCV	SCV PDS	100	25	5	500

The Archon autosampler introduces 1 uL of the Surrogate Spike Solution to each sample at 625 µg/mL in P&T methanol for a final concentration of 125 µg/L.

7.4 Supplies

- pH paper (pH 0-14 range).
- Sand, white quartz - Aldrich Cat # 27,473-9, or equivalent.
- Gas-tight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 25-mL, and 50-mL).
- Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.
- Sparge Tubes - 18 mm x 150 mm Disposable Culture Tubes, VWR no. 60825-673 or equivalent.
- Stainless steel spatulas

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Note: If the instrument is equipped with a functioning PID, the detector should be calibrated for the surrogate. The information provided by the more selective detector can be used to verify that the purge and trap device is working properly even in the presence of significant hydrocarbons. However, the surrogate should always be reported from the FID; the PID calibration is not required for method control (i.e. do not stop analysis or rerun samples for PID failure).

Set up instruments using operating parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements and chromatographic practice. Use a sparge volume of 5 mL.

Enter data into ChemStation using file naming conventions provided in Appendix E.

Bake the trap (when using the OI concentrator, ensure an empty sparge tube is mounted on the autosampler at the selected position) and the GC oven for at least 14 minutes each day before samples are analyzed.

Prior to analyzing calibration, QC, or field samples make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

8.2 Calibration and Standardization

The calibration standards preparation is detailed in Section 7.3.1

Set up the purge and trap concentrator for water analysis ensuring that the sparge needles reach to within 5 mm of the bottom of the sparge cells. The same calibration is used for the analysis of both water and soil methanol extracts.

8.2.1 Initial Calibration

Perform an initial calibration using the WDS standard and a minimum of five calibration standards to establish an external standard linear calibration using the average calibration factor. Refer to Section 9.3.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Check that compound type in ChemStation is set to H. This setting sums the area between the start and end of the analyte range. The chromatogram from the WDS standard will be used to set the start and stop integration times in ChemStation.

Analyze each of the standards and instrument blanks as described in Section 8.3.1. An example initial calibration sequence appears below:

	Sample Name		Sample Name
1	IB	6	1,000 µg/L gasoline
2	500 µg/L WDS standard	7	2,000 µg/L gasoline
3	50 µg/L gasoline (QLS)	8	IB
4	100 µg/L gasoline	9	500 µg/L gasoline SCV
5	500 µg/L gasoline (CCV)		

Spike the water with the appropriate amount of primary dilution standard for the specific calibration solution being analyzed. See Section 7.3.1 for details.

Inspect the WDS standard and update start and stop integration times in the method to correspond to the 2-methylpentane and 1,2,4-trimethylbenzene peaks in the WDS standard. Quantitate each calibration standard and samples using this retention time range.

Update each level of the ChemStation ICAL method. All target analyte and surrogate responses in the ICAL method should be replaced with the new responses.

Print a ChemStation Response Factor Report. See Appendix C for QC limits.

Print page 3 of the ChemStation ICAL for gasoline to show that the method was updated correctly.

Print the ChemStation initial calibration compound list report to verify that the average calibration factor is used.

Save the method as outlined in Appendix E (ChemStation File Naming Conventions).

Analyze a SCV standard immediately after each initial calibration. See Section 9.3.1 of this SOP for frequency and Appendix C for QC limits.

If the initial calibration, the SCV, and the IB meet all criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples.

As needed, analyze other hydrocarbons such as Turpentine, Stoddard Solvent, Mineral Spirits, Naphtha, and Lacquer Thinner at 500 µg/L with each ICAL. These standards are used for identification purpose only. Use stock solution such as AccuStandard # HS-004S-40X, HS-005S-40X, HS-002S-40X, HS-003S-40X, and HS-001S-40X or equivalent.

8.3 Sample Analysis

Check that the LIMS ID and client sample ID on the vials coincide with the numbers on the LIMS Work Order to ensure that the correct sample is being analyzed.

If the sample has an unusual color, or other physical characteristic such as more than one phase, the presence of a precipitate, unusual viscosity, or physical signs of contamination a screening analysis is required to protect the analytical system from damage or contamination and to determine the appropriate subsequent dilution. If an initial screening is necessary, analyze the sample at a 1:50 dilution, unless the group

leader or Technical Director specifies otherwise. Document observed anomalies in the LIMS MMO field.

Note in the LIMS MMO field in the work order window if there is headspace present in the sealed sample vial. If the bubble exceeds 6 mm in diameter, data qualification may be required.

8.3.1 Water Sample Preparation

- Allow the samples to reach ambient room temperature before analysis.
- Break the chain of custody seal on the vial with a scalpel or other appropriate implement, and note if the seal is missing or compromised in any way.
- Fill a 5-mL syringe with the sample. Invert the syringe, remove any air bubbles, and bring the level to 5-mL by displacement with the plunger. Place any excess sample displaced from the syringe in the aqueous waste containers.
- Prepare MS, MSD, and LCS samples by spiking with the analytes of interest. Add 25 µL of the 100 µg/mL gasoline water matrix spike/LCS solution to the matrix spike sample to prepare an MS/MSD or to reagent water to prepare an LCS.
- If using OI autosampler, spike the water with 5 µL of the 125µg/mL surrogate solution. Attach the syringe to the Luer lock mount on the purge and trap concentrator. Open the mount valve, inject the contents of the syringe into the sparge cell, and close the valve. Remove the syringe from the mount. Rinse the syringe with DI water after each sample.
- If using the Archon autosampler, load the samples in the Archon autosampler. The autosampler will add surrogate.
- Check the pH of the sample using pH 0-14 range pH paper. Record the pH in the injection logbook. Note any samples that have a pH greater than 2 in the LIMS MMO field in the work order window.

8.3.2 Soil Sample Preparation

This section contains procedures for the extraction and analysis of soil samples collected as bulk samples in glass jars or other containers (see Section 5.1 for documentation requirements when bulk samples are received), in EnCore™ sampler devices, or pre-weighed vials preserved in the field with methanol.

The typical sample weight is 5 g (nominal).

The percent moisture is determined from a separate aliquot as described in EPA Region 9 Laboratory SOP 460, *Percent Moisture Determination*.

To prevent the loss of certain volatile organics the sample must not be allowed to reach room temperature. The following steps must be taken as rapidly as possible to prevent loss of volatile components. Have the LIMS benchsheet prepared and all vials, standards, etc. ready prior to beginning the next steps.

1. Remove the sample from the refrigerator immediately prior to extraction or analysis. Samples should be extracted as soon as possible after receipt and within 48 hours of collection even if analysis will not to be performed immediately.

2. Break the chain of custody seal on the container with a scalpel or other appropriate implement, again making note in the logbook if the seal is missing or compromised in any way. Observe the sample closely for evidence of contamination. If the sample appears to contain hydrocarbons (an oily appearance or sheen) the sample must be analyzed at a dilution to prevent damage to the analytical system.

3. To extract bulk samples, use a stainless steel spatula. Immediately transfer approximately 5 g into a 20-mL tared vial. Record the weight of soil added to the container to the nearest 0.01 g in the LIMS bench sheet. If possible, all samples within a sample delivery group should be extracted at the same time along with the MB preparation.

4. To extract samples collected with the EnCore™ sampling device, transfer the contents of the EnCore™ sampler into a 20-mL tared vial. Record the weight of soil added to the container to the nearest 0.01 g in the LIMS bench sheet.

5. Quickly add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate stock solution to the vial. Spike MS/MSD samples with 5 uL of the Gasoline Stock Standard containing 50,000 µg/mL of gasoline. Cap the vial and vortex for 30 seconds. These steps must be done rapidly in order to prevent the loss of volatile organics from the sample.

6. Prepare a soil LCS by spiking 5 g of reagent sand in a 20-mL vial with 5 uL of the Gasoline Stock Standard containing 50,000 µg/mL of gasoline. Add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate spike solution to the vial. Cap the vial and vortex for 30 seconds.

7. Prepare a soil MB using 5 g of reagent sand in a 20-mL vial. Add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate spike solution to the vial. Cap the vial and vortex for 30 seconds.

8. Transfer approximately 1 mL of each extract to a GC vial for storage in the laboratory freezer at ≤-10 °C. Extracts must be analyzed within 14 days from sample collection. Use this extract for the analysis and any subsequent dilutions that may be necessary.

9. Weigh samples collected in pre-weighed containers preserved in the field with methanol to the same level of precision as the weight recorded on the chain-of-custody or vial (0.1 g or 0.01 g). Enter the vial and methanol weight (the pre-weight) from the chain-of-custody or vial in the LIMS bench sheet and calculate the sample weight by subtraction. Quickly add soil surrogate spike solution to the vial at the rate of 2.5 µL per mL of methanol.

10. If using OI autosampler, analyze 100 µL of the extract in 4.9 mL of reagent water according to the instructions for 5-mL water analysis in Section 8.3.1.

11. If using Archon autosampler, analyze 1mL of the extract to 49 mL of reagent water in a syringe. Mix and transfer the resulting solution to a 40 ml VOA vial and loading the vial onto the Archon autosampler. MAKE SURE TO USE A SOIL METHOD WHICH DOES NOT ADD ADDITIONAL SURROGATE.

8.3.3 Analytical Sequence and Sample Analysis

Set up a ChemStation data acquisition sequence from the LIMS sequence using the GC operating parameters in Appendix D. Include the client sample ID and the laboratory sample ID in the sample description field. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials. Enter this sequence in the instrument run log, if used.

For water analysis:

1. The method defaults are 5 mL sample, 5 mL final volume, and dilution factor 1. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 mL and 5 mL respectively.
3. In the bench sheet, the sample the initial and final volumes default to 5 mL.
4. Edit the bench sheet initial volume for samples and QC to reflect the actual volumes used.
5. When setting up the ChemStation sample sequence, enter 1 as the dilution factor in the multiplier field

For Soil analysis:

1. The method defaults are 5 g sample, 5 mL final volume, and dilution factor 100. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 g and 5 mL, respectively. (Note that the 5 mL volume represents the purge volume not the methanol extract volume.
3. In the bench sheet, the sample weight defaults to 5 g. Edit the initial weight to the actual weight used as needed.
4. Edit the bench sheet final volumes for samples and QC from 5 mL to the actual of methanol used to extract the samples (which is usually 10 mL).
5. When setting up the ChemStation sample sequence, enter 50 as the dilution factor in the multiplier field. (Do not apply the multiplier field to sample or surrogate results in ChemStation; LIMS does this later). The dilution factor, D = syringe volume/methanol extract volume in the syringe. This is typically 50 mL/1 mL = 50. If a greater dilution is required, calculate the dilution factor based on the volume of methanol used, e.g. for 100 uL, D is 50 mL/0.1 mL = 500.

See Section 9.4 for batch quality control (QC) frequency and corrective action requirements. It is highly recommended that the MB, LCS, and MS/MSD be analyzed as early as possible in the analysis of a batch.

If the initial calibration, the SCV, and the IB meet all criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples.

Example Field Sample Analysis Sequence:

	Sample Name		Sample Name
1	IB	6	MS (as needed)
2	500 µg/L gasoline CCV	7	MSD (as needed)
3	50 µg/L gasoline QLS	8-18	Field samples (as needed)
4	MB	19	IB
5	LCS	20	500 µg/L gasoline CCV

Enter the first and last sample positions in the concentrator and, with the ChemStation software in data acquisition mode, press the start button on the concentrator to begin purging the first sample. The purge and trap concentrator parameters are found in Appendix D.

When possible or if there are indications that the sample may foam, observe the initial purging. If the sample does foam, it can be analyzed as long as the foam does not enter the sparge vessel neck and enter the transfer line leading to the trap.

If it appears that the sample will foam excessively, discontinue the purging by pressing the [2nd], [on], and [enter] keys. Drain the sparge cell; rinse it with methanol, then reagent water. Place the sample waste and rinsate in the aqueous waste container. Bake out the trap and the GC for 25 minutes before analyzing additional samples. Analyze reagent water blank to show that the sampler is free from contamination before analyzing sample.

Analyze the sample at a 1:10 dilution, or other appropriate dilution to prevent foaming even though the detection limits are elevated. Document any sample foaming in the run log and the LIMS WO MMO field.

8.3.4 Analyte Identification and Quantitation

Update the center of the retention time window for the surrogate by using the absolute retention times from the calibration verification standard at the beginning of the analytical shift. Establish the ChemStation window as ± 0.06 minutes (peaks that drift more than 0.03 minutes will be flagged "f" by the data system as possible false positive).

All surrogates in the field and QC samples must fall within the ± 0.03 minute retention time window or the analyst must reject the analysis or review and accept the data with a written comment such as "retention time shift due to high concentration of interfering hydrocarbon".

If the retention time does not fall within the retention time window and no source of drift is identified, then take corrective action to restore the system. If repairs to the system are required then a new initial calibration must be performed.

Review the sample chromatograms for appropriate qualification. Several situations are routinely encountered:

- The chromatographic pattern resembles the standards; proceed with quantitation and reporting.
- The chromatogram differs markedly from the standard; visually compare the sample chromatogram to available hydrocarbons analyzed with the initial calibration. Software tools such as overlaying various standard chromatograms on the sample chromatogram should be employed when helpful or to support the qualification. Use the WO Memo field and/or appropriate qualifier flags (F1, J) to report the data. A comment such as "hydrocarbon pattern does not resemble available standards" with a list of those hydrocarbon mixtures may be appropriate.

- The majority of the area is due to a single-component and not a hydrocarbon mixture; consult the group leader and/or technical director to determine if the peak should be excluded from the quantitation. Use the WO Memo field and appropriate qualifier flags (F1, J) to report the data.
- The client has requested qualitative review against various standards; refer to the TDF and project notes to determine the project specific analysis and reporting procedures. This may include calibrating with a source supplied by the client, review against numerous standard chromatograms, or other procedures. Always document this process in the WO Memo field and in the data package and report as necessary

Quantitate the sample data using the ChemStation software using the appropriate initial calibration mean CFs. Quantitate methanolic extracts of soil samples with the same initial calibration used to quantitate water samples. If applicable, indicate degree of similarity of sample chromatogram to the gasoline standard. Print out quantitation reports and chromatograms for each field and QC sample.

LIMS calculates final analyte concentrations in samples. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

8.3.4.1 Water Calculations

Calculate target analyte concentrations in aqueous samples using Equation 1.

Equation 1:

$$\text{Concentration (ug/L)} = \frac{A_x \times DF}{RF}$$

Where:

A_x = area response for analyte x
DF = dilution factor
RF = mean response factor from the initial calibration (area/concentration)

8.3.4.2 Soil Calculations

Calculate target analyte concentrations in soil samples using Equation 2.

Equation 2:

$$\text{Concentration (mg/Kg dry weight basis)} = \frac{A_x \times V_t \times DF \times V_p \times 1{,}000}{RF \times W \times D \times V_i \times 1{,}000}$$

Where:

A_x = area response for analyte x
D = dry weight factor (Percent solids/100)
W = weight of sample in grams
RF = mean response factor from the initial calibration (area/concentration)
V_t = total volume of extract in mL (see note)
DF = dilution factor (volume of water divided by volume of extract (nominally 5 mL / 0.1 mL or 50)
V_i = volume of extract injected in µL
Vp = volume of extract purged in mL (i.e. 5 mL)
1,000 (in numerator) 1000 µL = 1 mL
1,000 (in denominator) 1000 mL = 1 L

Yields concentration units of µg/g = mg/Kg

Note: V_t is equal to the volume of methanol (see benchsheet) plus the volume of water from the solid calculated as (1-%solid) * W. See EPA Region 9 Lab SOP 460 for percent solids determination.

8.3.5 Manual Integration

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the sample components. If in the judgment of the analyst, it does not, then correct the integration using the ChemStation QEDIT software module. Document manual integrations, if any, following the procedure described in USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

8.3.6 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Target analyte results must be within range of initial calibration.
- Process and review the results for the IB, CCV, and QLS instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and QLS QC sample results are within QC limits. See Section 9.3 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.4 for batch QC requirements.

- Check that surrogate compound retention times are within the window specified in Section 9.5.1 and Appendix C. Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.5 for sample QC requirements.

- Review all sample results to determine if any samples need to be re-analyzed at a dilution. If any of the target compounds in soil extract or water samples exceed the initial calibration range of the instrument, dilute by using a smaller aliquot of the water sample or soil extract combined with reagent water to a total volume of 5 mL.

- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.7 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool.

1. Copy data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and for archiving.

2. Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using Data Tool.

3. After making an empty upload file containing the samples analyzed in the LIMS batch or sequence, import and merge the data files using the LIMS Data Tool module. Load the resulting merged data file into the LIMS Data Entry/Review table.

Review final results in the LIMS. Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).

- Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

- In order to take the dilution that occurs during soil sample preparation into account, the dilution factor for undiluted soil samples in the LIMS Data Entry/Review table must be 50. Any actual sample dilutions must be

multiplied by 50 to obtain the effective sample dilution to be entered in LIMS. Edit dilutions in DataTool or LIMS entry table as needed.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix F.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 Purge and trap maintenance

Symptom:

- Carryover
  Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.
  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all purged analytes.
  Possible cause: Leak in system.
  Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom:

- Carryover
  Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: as necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

9.1 Retention Time Windows

- Establish retention time windows for the surrogate whenever a new GC column is installed or a new DOC is required on each chromatographic column and instrument.

- Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed.

- Make three injections of the CCV level calibration standard over the course of at least a 72 hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too narrow.

- Record the retention time to three decimal places (e.g., 9.007) from three injections.

- Calculate the mean and standard deviation of the three absolute retention times. If the standard deviation of the retention times for a target compound is less than 0.01 minutes then use a default standard deviation of 0.01 minutes.

- The width of the retention time window is defined as ±3 times the standard deviation of the mean retention time. If the default standard deviation is employed, the width of the window will be ±0.03 minutes. Set the ChemStation window to ±6 times the standard deviation so the software will identify peaks within the wider window and flag those which exceed the retention time window with the "f" flag (the flag is added to peaks outside one half the window) to prevent false negatives.

- For samples run during the same shift as an initial calibration, use the retention time of each analyte and surrogate in the mid-point standard of the initial calibration as the center of the retention time window.

- The first successful CCV of each daily sequence is used to establish the retention time around which the windows are calculated for that sequence. Update the retention time for each analyte in the ChemStation method. Updating the retention time windows will cause the "Last Update time" stamp to change. Save the method using today's date and utilize this method in quantitating today's runs. Print ICAL summary from the ICAL method and today's method to establish that the response factors did not change.

- Document the RT window calculations in a spreadsheet and store them in the laboratory where the samples are analyzed. Provide a copy to the Laboratory QAO.

9.2 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency* for more details.

9.3 Instrument QC

9.3.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed

The GC system must be calibrated whenever corrective action that changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- The data system calculates the calibration factor (CF) using Equation 3.

  Equation 3

  $$CF = (A_x)/ (C_x)$$

  Where
  Ax = Area of analyte x, or area sum response of gasoline
  Cx = Concentration of the standard injected (µg/L)

- The data system calculates the percent relative standard deviation (%RSD) of the CF values for each analyte using Equation 4.

  Equation 4

  $$\%RSD = (SD/ CF_{avg}) \times 100$$

  Where SD is the sample standard deviation and is calculated as:

  $$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - CF_{avg})^2}{n-1}}$$

  Where:
  CF_{avg} = Mean calibration factor from the initial calibration.
  CF_i = Calibration factor for a calibration level.

- Print a ChemStation Response Factor Report. Verify that the %RSD of the target analytes and the surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

- Analyze an SCV sample immediately after each initial calibration. Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.

- Calculate the percent difference (%D) between the SCV CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.

  Equation 5:

$$\%D = \frac{CF_c - CF_{avg}}{CF_{avg}} x100$$

  Where:
  CF_c = SCV or CCV CF
  CF_{avg} = ICAL mean CF

- See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

9.3.2 Continuing Calibration Verification

- Analyze a CCV standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the CCV standard and ends with the injection of the last sample that can be injected within 12 hours of the beginning of the period.

- Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.

- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.

- The %D must be within QC limits. See Appendix C for QC. If an analyte fails this criterion a second calibration verification may be analyzed.

Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

If repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

- Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.3.3 Quantitation Limit Standard

- Analyze a quantitation limit standard (QLS) each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

- Calculate the concentration of the target analytes using Equation 1.

- Calculate the percent of true value (TV) for the target analytes using Equation 6.

  Equation 6:

  $$\% \text{ True Value} = (Cd / Tv) \times 100$$

  Where:
  Cd = Concentration determined by analysis
  Tv = True value of standard

- If the % TV is not within the QC limits in Appendix C, analyze a second QLS sample. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.3.4 Instrument Blank

- At a minimum, one acceptable IB is required for each 12-hour analysis period.

- Evaluate the IB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the IB results are not within QC limits, analyze a second IB. If the second IB also fails but the system is significantly cleaner, another IB may be analyzed; if not, take corrective action.

- Corrective action - If the IB is not acceptable the source of the contamination must be found and eliminated and the problem documented before analysis can proceed.

- Surrogate recovery is not evaluated for IB QC samples.

9.4 Batch QC

9.4.1 Method Blank

- Extract and analyze a method blank (MB) with each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system – from extraction through GC analysis – is free of contamination.

- For aqueous samples a MB is identical to an IB. For soil sample analysis it is necessary to prepare an extracted MB.

- If the surrogate recovery does not meet acceptance criteria, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action – if the MB result exceeds QC limits and the sample result is less than five times the MB analyte result, re-analyze the MB. If the MB result still exceeds QC limits then the MB and all associated samples must be re-prepared and re-analyzed. If the MB result exceeds QC limits and the sample result is ≥ five times the MB result or is not detected then report the sample result.

9.4.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.

- Calculate the percent recovery (%R) using Equation 7.

Equation 7:

$$\% \text{ Rec} = (\text{LCS}/\text{SA}) \times 100$$

Where,
LCS = LCS result
SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.4.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed for each batch of twenty or fewer samples extracted as a group. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. Do not choose any obvious field blanks as the QC sample.

- Calculate the recovery of each analyte using Equation 8.

Equation 8:

$$\% \text{ Rec} = ((\text{SSR} - \text{SR})/\text{SA}) \times 100$$

Where,
SSR = Spiked sample result
SR = Unspiked sample result
SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using Equation 9.

Equation 9:

$$\text{RPD} = \frac{(\text{MSC} - \text{MSDC})}{(\text{MSC} + \text{MSDC})/2} \times 100$$

Where,
MSC = Measured concentration of analyte in MS
MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

9.4.4 Storage Blank

- Every Monday morning, or the first workday of the week, fill three 40-mL screw-cap volatile vials with PTFE-faced silicone septum with reagent water, acidify to pH $\leq$ 2, and store them with the samples, in the sample storage refrigerator.

- Analyze storage blank (SB) once every week while samples are being stored waiting for analysis. The storage blank indicates whether contamination may have occurred during sample storage.

- If samples have been stored in the refrigerator during the previous week, analyze the storage blank the following Monday, or on the first work day of that week. If samples have not been stored in the refrigerator during the previous week, discard the blanks and place new storage blanks in the refrigerator.

- Evaluate the SB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the SB does not meet QC criteria all affected data must be qualified.

9.5 Sample QC

9.5.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

Equation 10:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.

- Take the following steps if surrogate recovery is not within the limits:

  1. If the system is equipped with a functioning PID, the second detector can be used to provide further information. If sample matrix is the source of the error, as demonstrated by acceptable surrogate recovery on the PID, document the issue in the WO MMO field and on the chromatogram, and continue. If not, proceed with troubleshooting.
  2. Ensure that there are no calculation errors, and check the system performance.
  3. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
  4. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case-by-case basis.

- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

- Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the matrix interference is confirmed and the sample does not need re-analysis.

- If the surrogate recoveries of the re-analysis of the extract are within limits, then:

  1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Mark the first chromatogram as "Not Reported, see re-analysis."

2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the LIMS WO MMO filed. Mark the first chromatogram as "Not Reported, see re-analysis."

3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction, mark the first chromatogram as "Not Reported, see re-analysis."

4. If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses.

9.6 Method Performance

Region 9 Laboratory performance for this procedure from February 23, 2009 to February 24, 2010 is summarized in the following table.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery,%	STD, % (σ)	95% Confidence Interval (2σ)
TPH as Gasoline	Water	LCS	30	94.4	6.48	81.5 - 107
TPH as Gasoline	Solid	LCS	43	95.8	13.3	69.3 - 122

The following functional areas of the SOP may be significant sources of analytical error:

- Poor purge efficiency due to specific analyte characteristics or other problems.
- Standard degradation
- Volatile compound losses in spike solutions and standards.

10 DOCUMENTATION

10.1 Standards

Record the preparation of all standards in the Element database. Include a copy of each Analytical Standard Record associated with sample analysis in the data package.

10.2 Analytical sequence

The analytical sequence is documented in the Element database in the instrument Run

Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, laboratory sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.3 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.5 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.6 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

Agilent Technologies EnviroQuant ChemStation User's Guide

HP 5890 Gas Chromatograph Users Manual

Agilent AG6890 Gas Chromatograph Users Manual

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U.S. Environmental Protection Agency Region 9 *Laboratory Quality Assurance Plan,* Revision 10, November 5, 2007.

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U.S. Environmental Protection Agency Region 9 SOP 460, *Percent Solids Determination*

U.S. Environmental Protection Agency Region 9 SOP 706, *Laboratory Waste Management Procedures*

U.S. Environmental Protection Agency Region 9 SOP 805, *Refrigerator Temperature Monitoring*

U.S. Environmental Protection Agency Region 9 SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*

U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures*

U.S. Environmental Protection Agency Region 9 SOP 840, *Notebook Documentation and Control*

U.S. Environmental Protection Agency Region 9 Laboratory SOP 880, *Demonstration of Capability*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The CF is area/concentration unit (µg/L) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Analyte	QL, on column, µg/L	QL, 5g Solid, mg/kg	QL, 5 mL Water, µg/L
TPH as gasoline	50	5.0	50

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC Measurement	Frequency	Criteria
Initial Calibration (ICAL) RSD	Instrument setup, after maintenance, and when CCV fails criteria	≤ 20
Second Source Verification (SCV) %D	After each ICAL	± 30
Calibration Verification (CCV) %D	Beginning of each daily sequence, every 12 hours, end of sequence	±20
Quantitation Limit Standard (QLS)	After first CCV of sequence, and after 40 samples.	± 40% of TV
Blanks :		< ½ QL
MB	Each batch of 20 or fewer samples	
IB	After each CCV	
SB	Once per week	
Laboratory Control Sample (LCS) %R	Each batch of 20 or fewer samples	Water: 75 - 114 Soil: 56 - 136
MS/MSD %R	Each SDG of 20 or fewer samples	Water:71 - 114 Soil: 72-108
MS/MSD RPD	Each SDG of 20 or fewer samples	Water:11 Soil: 20
Surrogate Recovery of QC and field samples (except IB) %R	Every samples	Water:76 - 121 Soil: 75 - 119
Retention Time Windows	Each CCV	±3 SD of RT Study*

*ChemStation window is ±6 SD of RT Study (SD is usually 0.01 min) and peaks are flagged at the more restrictive window.

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

OI 4560 Concentrator

Recommended operating settings for the OI 4560 purge & trap concentrator that is interfaced with the HP 5890 Series II GC and the DPM-16 autosampler is as follows.

PARAMETER	SETTING
Purge temperature	20°C
Sample temperature	ambient
Purge Time	11 minutes
Dry purge	2.3 minutes
Purge Flow	35 - 40 mL/min
Desorb	2.00 minutes @ 180°C
Bake	14 minutes @ 190°C
Valve temperature	100°C
Mount temperature	40°C
Line temperature	100°C
DPM16 transfer line	100°C
DPM Valve temperature	100°C
Water Management	ON
Purge Temperature	100°C
Desorb Temperature	20°C
Bake Temperature	240°C

HP 5890 Series II OR AG6890 Gas Chromatograph

PARAMETER	SETTING
Injector temperature	225°C
Column Equilibration time	0.5 minutes
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	10°C/minute
Final Oven Temp	250°C
Final Hold Time	0 minutes
Column Flow rate	~ 8 mL/min
Detector B (PID) Temp	280°C
Signal 1 (A)	FID
Signal 2 (B)	PID (If Present)
Column Flow	Constant (If applicable)
Split flow	20 mL (If applicable)
Split Ratio	2 (If applicable)

Recommended Purge and Trap Concentrator operating parameters

Tekmar 3000 Concentrator

The recommended operating method for the Tekmar 3000 A purge & trap concentrator which is interfaced with the AG6890 GC and Varian Archon Autosampler is as follows.

PARAMETER	SETTING
Standby temperature	32°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for medium-level/40°C for low-level
Purge Time	11 min
Dry purge	0.6 min
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	245 °C
Desorb	2 min @ 250 °C
Bake	10 min @ 260 °C
Auto drain	On
Bake gas bypass	Off
Valve temperature	140 °C
Mount temperature	40 °C
Line temperature	140 °C
Bottom of trap temperature	NA

Varian Archon Autosampler

The recommended operating method for the Archon autosampler which is interfaced with the Tekmar 3000 and the HP5973 GC/MS is as follows.

PARAMETER	SETTING
Valve temperature	100 °C
Line temperature	110 °C

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:
Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS
Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods
Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence
For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:
Data: I:\Room Number\Instrument\Year\MDDYS
Methods: I:\Room Number\Instrument\Methods
Sequences: I:\ Room Number\Instrument\Sequence

Methods
MDDYITA

Sequence
MDDYS

Data Files
For GC:
MDDYICSS

For GC/MS
MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane	X
504	E
TO15	A
BNA	B
BNA-L (SIM)	L
Congeners	C
P/P	P
PCB	P
RSK175	R

Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 580-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3, ….

T: Matrix Type (if applicable)

Water	W
Solid	S
Air	A
Oil	O
Other	X

Y: Year i.e. 5 for 2005

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	As Needed	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	As Needed	Replace with liner or with signs of wear.
Inlet septum	As Needed	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.
Purge/Sample Lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.

Item	Frequency	Actions/Comments
PID	Annually or as needed	Clean window

APPENDIX G.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
EPA Review Form
ESAT technical review guide
Discrepancy Reports (if applicable)
Work Order Memo (if applicable)
Daily folder review forms or checklists
Analysis matrix listing all analytical runs

Tracking Forms
- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)
- Bench Sheets (and extraction logs, where used)
- Sample cleanup data and records (e.g., GPC logs)
- Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s), where not used in the Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:
- Initial Calibration Data
- Sample Data

Miscellaneous Data
- Other data as applicable (e.g., conductivity for perchlorate)

Standard Records
Standards records from LIMS (and logbook pages as needed

APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 380
Revision: 6, Effective: 03/01/2010

PURGEABLE AROMATICS AND HYDROCARBONS BY GC PID/FID

Revision	Effective Date	Description
6	06/26/09	Revised to remove reference to the analysis of BTEX and MTBE and to comply with current SOP format and recent changes to internal COC requirements. Minor edits throughout.
7	03/01/10	Added the use 2-methylpentane and 1,2,4-trimethylbenzene as the window defining standard for the integration of gasoline. Added the use of Tekmar/Archon autosampler. Updated to reflect 8015C requirements.